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Kinetic model of hyperbranched polymers formed by the polymerization of AB_2 monomer with a substitution effect

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Abstract

Hyperbranched polymers obtained by the polymerization of AB_2-type monomer with a substitution effect on the B_2 groups were studied by means of the kinetic model. In this polymerization with the substitution effect, if one of the B_2 group reacts first, the reactivity of the remaining unreacted B group will be changed. The profiles of the degree of polymerization, polydispersity, degree of branching, and structural units of the hyperbranched polymers with the conversions were all calculated by the generating function method. It is shown that the weight-average degree of polymerization and the degree of branching of the hyperbranched polymers having substitution effect differ from that with equal reactivity of the B_2 groups. If the substitution effect causes an increase in the rate constant after one of the B_2 groups has reacted, a broader molecular weight distribution and a higher degree of branching are observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched polymer; Substitution effect; Generating function

1. Introduction

Hyperbranched polymers can be synthesized by a simple one-pot polymerization, e.g. polycondensation of AB_x-type monomers with or without AB monomers, where x is greater than or equal to two [1–7]; self-condensing vinyl polymerization [8]; and radical alternating copolymerization [9]. In addition, a large variety of monomers with different functional groups are available [10–12]. In contrast to dendrimers with a perfectly regular structure, hyperbranched polymers contain randomly branched and some linear structures. It is important to develop adequate theoretical models to understand the dependence of the molecular weight, polydispersity index (PDI) and degree of branching on polymerization condition, and to construct the formation-structure–property relationships of these novel polymers [13,14].

With the help of statistical theories, Stockmayer [15,16], Flory [17,18] and Gordon et al. [19–21] derived the basic relations between the structure formation, such as molecular weight of polymers, and the extents of reaction for nonlinear polymerizations. Moreover, Frey and coworkers, and Moller et al. showed that the degree of branching, a very important structural parameter in characterizing the hyperbranched polymers, can be calculated by the statistical model for the polycondensation of AB_x monomer and the copolymerization of two monomers AB_x with AB_y [22–25]. In addition, a kinetic model of the polycondensation of AB_x-type monomer with B_f cores has been established to examine the molecular weight distribution (MWD) of hyperbranched polymers [26–28]. In the previous study, we also adopted a kinetic model to investigate the effects of different amounts of cores with various reactivities on the molecular weight and the degree of branching during the polymerization [29].

Most theoretical models for polymerization of AB_x monomer are base on the assumption that all functional groups of the same type are equally reactive, and react independently of one another. In other words, all the B groups in the AB_x monomer have the same reactivity. Yet, the equal reactivity is questioned if the substitution effect is taken into account owing to the steric effects or other reasons [30,31]. Therefore, in a polymerization with a substitution effect, the reactivity of unreacted groups

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depends on the number of already reacted on the same unit. In the literature, the effects of the different reactivities on the microstructures of hyperbranched polymers were examined by Monte Carlo simulations [32,33]. Although the computer simulation can provide detailed information of the microstructures, the results determined by the finite simulation system may be different from that by an infinite system.

In this work, we extend the generating function method [34–38], based on the kinetic theory, to the polymerization of AB_2 monomer with the substitution effect. This kinetic model is adopted to examine the effects of reactivity ratio on the average degree of polymerization, polydispersity, degree of branching, and structural units of the hyperbranched polymers.

2. Kinetic model of polymerization of AB_2 with substitution effect

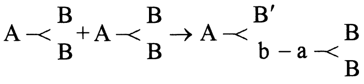
A polycondensation system is considered with an AB_2 monomer, which contains one reactive A group and two reactive B groups. The two B groups are equally reactive until one of them reacts, by which the substitution effect results in the change of the reactivity of the unreacted B group, and denoted as B′. The substitution effect caused by the A group is not taken into account in this study. The effects of intramolecular reactions on the structure parameters of the hyperbranched polymers are also important for several cases discussed before [39,40]. However, in this study, we focus on the substitution effect, and assume that the reaction is bimolecular, and there are no cyclization occurs during polymerization; then every molecule is treelike, and contains one unreacted A group and many unreacted B and B′ groups. Either B or B′ groups can react with an A group on the other molecule but in different rate constants.

$$A + B_2 \overset{2k_{AB}}{\rightarrow} a + B'b \qquad (1)$$

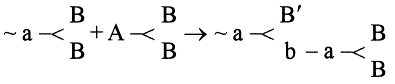
$$A + B'b \overset{k_{AB'}}{\rightarrow} a + b_2 \qquad (2)$$

where k_{AB} and $k_{AB'}$ are the reaction rate constants, and a, B′b, and b_2 represent the reaction products of A, B_2, and B′b, respectively.

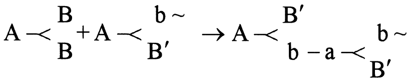
The reactions between various structural units (not functional groups or molecules) can be written in the following kinetic scheme


$$A\prec\substack{B\\B} + A\prec\substack{B\\B} \rightarrow A\prec\substack{B'\\b-a\prec\substack{B\\B}}$$

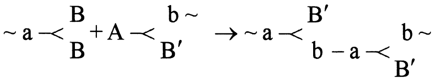
$$G(1) + G(1) \overset{2k_{AB}}{\rightarrow} G(2) + G(3)$$


$$\sim a\prec\substack{B\\B} + A\prec\substack{B\\B} \rightarrow \sim a\prec\substack{B'\\b-a\prec\substack{B\\B}}$$

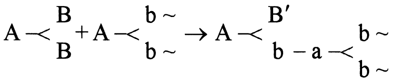
$$G(3) + G(1) \overset{2k_{AB}}{\rightarrow} G(4) + G(3)$$


$$A\prec\substack{B\\B} + A\prec\substack{b\sim\\B'} \rightarrow A\prec\substack{B'\\b-a\prec\substack{b\sim\\B'}}$$

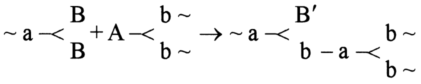
$$G(1) + G(2) \overset{2k_{AB}}{\rightarrow} G(2) + G(4)$$


$$\sim a\prec\substack{B\\B} + A\prec\substack{b\sim\\B'} \rightarrow \sim a\prec\substack{B'\\b-a\prec\substack{b\sim\\B'}}$$

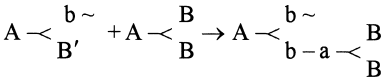
$$G(3) + G(2) \overset{2k_{AB}}{\rightarrow} G(4) + G(4)$$


$$A\prec\substack{B\\B} + A\prec\substack{b\sim\\b\sim} \rightarrow A\prec\substack{B'\\b-a\prec\substack{b\sim\\b\sim}}$$

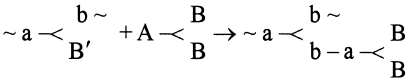
$$G(1) + G(6) \overset{2k_{AB}}{\rightarrow} G(2) + G(5)$$


$$\sim a\prec\substack{B\\B} + A\prec\substack{b\sim\\b\sim} \rightarrow \sim a\prec\substack{B'\\b-a\prec\substack{b\sim\\b\sim}}$$

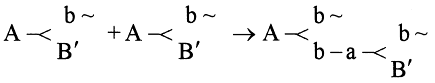
$$G(3) + G(6) \overset{2k_{AB}}{\rightarrow} G(4) + G(5)$$


$$A\prec\substack{b\sim\\B'} + A\prec\substack{B\\B} \rightarrow A\prec\substack{b\sim\\b-a\prec\substack{B\\B}}$$

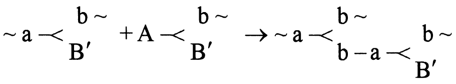
$$G(2) + G(1) \overset{k_{AB'}}{\rightarrow} G(6) + G(3)$$


$$\sim a\prec\substack{b\sim\\B'} + A\prec\substack{B\\B} \rightarrow \sim a\prec\substack{b\sim\\b-a\prec\substack{B\\B}}$$

$$G(4) + G(1) \overset{k_{AB'}}{\rightarrow} G(5) + G(3)$$


$$A\prec\substack{b\sim\\B'} + A\prec\substack{b\sim\\B'} \rightarrow A\prec\substack{b\sim\\b-a\prec\substack{b\sim\\B'}}$$

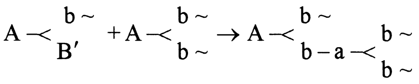
$$G(2) + G(2) \overset{k_{AB'}}{\rightarrow} G(6) + G(4)$$


$$\sim a\prec\substack{b\sim\\B'} + A\prec\substack{b\sim\\B'} \rightarrow \sim a\prec\substack{b\sim\\b-a\prec\substack{b\sim\\B'}}$$

$$G(4) + G(2) \overset{k_{AB'}}{\rightarrow} G(5) + G(4)$$

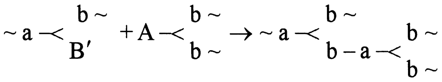
Table 1
The parameters of b_{ij} and k_i

$$\begin{bmatrix} b_{11} & b_{12} & b_{13} & b_{14} & k_1 \\ b_{21} & b_{22} & b_{23} & b_{24} & k_2 \\ b_{31} & b_{32} & b_{33} & b_{34} & k_3 \\ b_{41} & b_{42} & b_{43} & b_{44} & k_4 \\ b_{51} & b_{52} & b_{53} & b_{54} & k_5 \\ b_{61} & b_{62} & b_{63} & b_{64} & k_6 \\ b_{71} & b_{72} & b_{73} & b_{74} & k_7 \\ b_{81} & b_{82} & b_{83} & b_{84} & k_8 \\ b_{91} & b_{92} & b_{93} & b_{94} & k_9 \\ b_{10\,1} & b_{10\,2} & b_{10\,3} & b_{10\,4} & k_{10} \\ b_{11\,1} & b_{11\,2} & b_{11\,3} & b_{11\,4} & k_{11} \\ b_{12\,1} & b_{12\,2} & b_{12\,3} & b_{12\,4} & k_{12} \end{bmatrix} = \begin{bmatrix} 1 & 1 & 2 & 3 & 2k_{AB} \\ 3 & 1 & 4 & 3 & 2k_{AB} \\ 1 & 2 & 2 & 4 & 2k_{AB} \\ 3 & 2 & 4 & 4 & 2k_{AB} \\ 1 & 6 & 2 & 5 & 2k_{AB} \\ 3 & 6 & 4 & 5 & 2k_{AB} \\ 2 & 1 & 6 & 3 & k_{AB'} \\ 4 & 1 & 5 & 3 & k_{AB'} \\ 2 & 2 & 6 & 4 & k_{AB'} \\ 4 & 2 & 5 & 4 & k_{AB'} \\ 2 & 6 & 6 & 5 & k_{AB'} \\ 4 & 6 & 5 & 5 & k_{AB'} \end{bmatrix}$$



$$\mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}'\end{matrix} + \mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix} \rightarrow \mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}\end{matrix}$$

$$\mathrm{G}(2) + \mathrm{G}(6) \overset{k_{AB'}}{\rightarrow} \mathrm{G}(6) + \mathrm{G}(5)$$



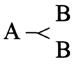
$$\sim\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}'\end{matrix} + \mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix} \rightarrow \sim\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}\end{matrix}$$

$$\mathrm{G}(4) + \mathrm{G}(6) \overset{k_{AB'}}{\rightarrow} \mathrm{G}(5) + \mathrm{G}(5)$$

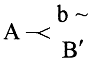
or

$$\mathrm{G}(b_{i1}) + \mathrm{G}(b_{i2}) \xrightarrow{k_i} \mathrm{G}(b_{i3}) + \mathrm{G}(b_{i4}) \qquad i = 1, 2, \ldots, 12 \qquad (3)$$

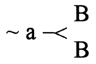
where

G(1) =  monomer

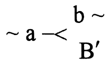
$$\mathrm{G}(1) = \mathrm{A}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix} \text{ monomer}$$

G(2) = 

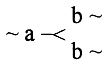
$$\mathrm{G}(2) = \mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}'\end{matrix}$$

G(3) = 

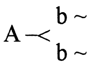
$$\mathrm{G}(3) = \sim\mathrm{a}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}$$

G(4) = 

$$\mathrm{G}(4) = \sim\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}'\end{matrix}$$

G(5) = 

$$\mathrm{G}(5) = \sim\mathrm{a}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}$$

G(6) = 

$$\mathrm{G}(6) = \mathrm{A}{\prec}\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}$$

The corresponding parameters, b_{ij} and k_i, are shown in Table 1, and

$$\rho = k_{AB'}/k_{AB} \qquad (4)$$

in which ρ is assumed to be a constant and independent of the extent of reaction. Furthermore, a vector **E** is defined to characterize the molecule $\langle E \rangle$

$$\mathbf{E} = (e_1, e_2, e_3, e_4, e_5, e_6, e_w) \qquad (5)$$

where e_J represents the number of structural units G(J) on a molecule $\langle E \rangle$, and e_w, equal to e_7, is the molecular weight of the molecule $\langle E \rangle$. For example, $\mathbf{E} = (1, 0, 0, 0, 0, 0, W(\mathrm{AB}_2))$ denotes monomer AB_2, and $W(\mathrm{AB}_2)$ is the molecular weight of this monomer; the molecule AB′ b-aB$_2$ formed by combining two AB_2 monomers can be specified by $\mathbf{E} = (0, 1, 1, 0, 0, 0, 2W(\mathrm{AB}_2))$, in the case of there are no condensates produced during the polymerization.

According to the mean-field theory, the effects of configuration and conformation are not considered in the calculation. Assuming that all reactions are chemically controlled, and there are no intramolecular reactions [13, 18], the reactions between molecules are

$$\langle E' \rangle + \langle E'' \rangle \xrightarrow{k_i} \langle E' + E'' + L_i \rangle \qquad i = 1, 2, \ldots, 12 \qquad (6)$$

where $\langle E' + E'' + L_i \rangle$ is the molecule formed by combining $\langle E' \rangle$ with $\langle E'' \rangle$ in the ith reaction, and

$$L_i = (l_1, l_2, \ldots, l_6, 0)$$

$$l_J = -\delta(b_{i1}, J) - \delta(b_{i2}, J) + \delta(b_{i3}, J) + \delta(b_{i4}, J), \qquad (7)$$

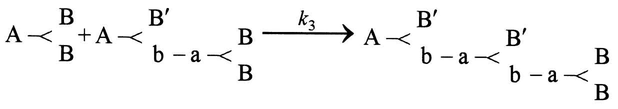
$$J = 1, 2, \ldots, 6$$

in which $\delta(b_{ij}, J)$ is Kronecker delta; that is

$$\delta(b_{ij}, J) = 1, \quad \text{for } b_{ij} = J$$

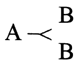
$$\delta(b_{ij}, J) = 0, \quad \text{for } b_{ij} \neq J$$

For example, a monomer AB_2 reacts with another dimer AB′ b-aB$_2$ as follows

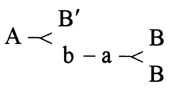


$$\mathrm{A}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix} + \mathrm{A}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}\end{matrix} \xrightarrow{k_3} \mathrm{A}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}\end{matrix}\end{matrix}$$

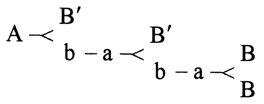
then

<E'> = 

$$\langle E' \rangle = \mathrm{A}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}$$

<E"> = 

$$\langle E'' \rangle = \mathrm{A}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}\end{matrix}$$

<E' + E" + L$_i$> = 

$$\langle E' + E'' + L_i \rangle = \mathrm{A}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}'\\ \mathrm{b}-\mathrm{a}{\prec}\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}\end{matrix}\end{matrix}$$

$$E' = (1, 0, 0, 0, 0, 0, W(\mathrm{AB}_2))$$

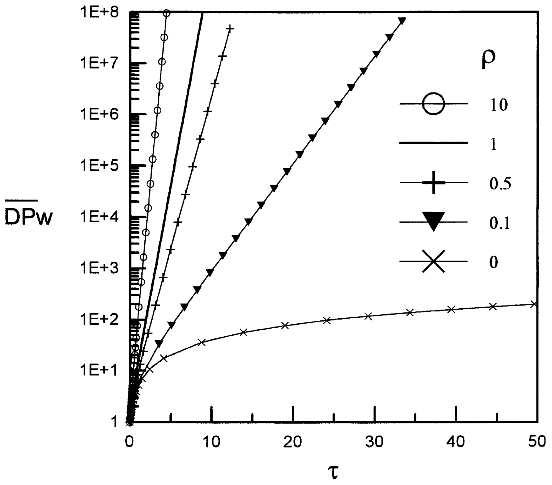


Fig. 1. Weight-average degree of polymerization versus reaction time for the systems with various rate constant ratios, ρ.

$$E'' = (0, 1, 1, 0, 0, 0, 2W(AB_2))$$

$$L_3 = (-1, 0, 0, 1, 0, 0, 0)$$

$$E' + E'' + L_3 = (0, 1, 1, 1, 0, 0, 3W(AB_2))$$

$$k_3 = 2k_{AB}$$

Furthermore, a dimensionless number fraction, $[E]$, the ratio of the reaction rate constant, k_i', and a scaled time, τ, are defined

$$[E] = N(E)/N_0 \tag{8}$$

$$k_i' = (k_i/k_0)(V_0/V) \tag{9}$$

$$\tau = tk_0(N_0/V_0) \tag{10}$$

where $N(E)$ is the number of isomers of the molecule $\langle E\rangle$; V is the volume of the reaction system; N_0, k_0, and V_0 are the arbitrary reference number, rate constant, and volume, respectively, and t is the reaction time.

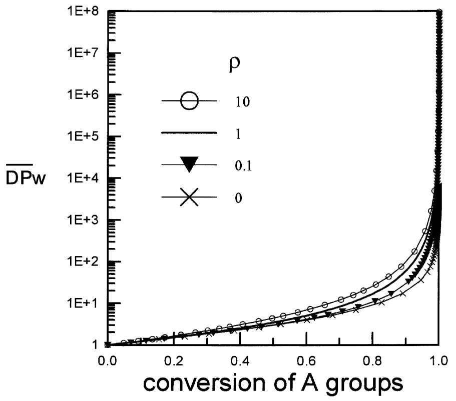


Fig. 2. Weight-average degree of polymerization versus conversion of A groups for the systems with various rate constant ratios, ρ.

If the change of the reaction volume is negligible; then according to Eq. (6), the rate equation of the isomers can be written as

$$\frac{d[E]}{d\tau} = \sum_{i=1}^{12} k_i' \left\{ \sum_{E'+E''+L_i=E} ([E'][E'']p_{i1}'p_{i2}'') - [E]p_{i1} \sum_{\text{all } E'''} [E''']p_{i2}''' - [E]p_{i2} \sum_{\text{all } E'''} [E''']p_{i1}''' \right\} \tag{11}$$

where $\sum_{\text{all } E}$ denotes the sum over all possible values of vector **E**, and $p_{ij} = e_J$ for $b_{ij} = J$. The one positive and two negative terms on the right side of Eq. (11) give the total rates of appearance and disappearance of the isomer $\langle E\rangle$, respectively. Eq. (11) cannot be solved directly, but it can be transformed into finite ordinary differential equations using a generating function [29,34–38]. The profiles of the average molecular weights of polymers and the fractions of the structural units, G(I), can be calculated from the generating function; the relevant algorithm is described in Appendix A.

3. Results and discussion

Figs. 1 and 2 show the profiles of the weight-average degree of polymerization, $\overline{DP}_w$, at different values of ρ, the rate constant ratio of the $k_{AB'}$ to k_{AB}. The weight-average degree of polymerization of the system with the higher value of ρ was found to increase more quickly than that with the lower one. All the $\overline{DP}_w$ curves tend to approach infinity at the complete conversion of A groups.

In the stepwise polymerization of AB_2 monomer, the relationship between the number-average degree of polymerization and the conversion of A group can be described as follows

$$\overline{DP}_n = \frac{\text{initial number of monomers}}{\text{total number of molecules during polymerization}} = \frac{N_0(AB_2)}{N_0(AB_2) - N_0(AB_2)\alpha(A)} = \frac{1}{1-\alpha(A)} \tag{12}$$

where $N_0(AB_2)$ is the initial number of AB_2 monomer; and α(A) is the conversion of A group. Obviously, as calculated by either Eq. (12) or the generating function method, the substitution effect does not influence the profiles of the number-average degree of polymerization.

If there is an increase in the rate constant after one of the B_2 groups has reacted, the rate constant ratio, ρ, is greater than one. As a result, the linear unit with group B′ reacts readily with another molecule, and forms an effective branching point and consequently a larger molecule. Because the larger molecule contains a higher number of the unreacted groups B or B′, it is easy to combine two large molecules into even larger one, and this causes a broad MWD of the hyperbranched polymers during polymerization as indicated in Fig. 3. In the extreme case that ρ equals

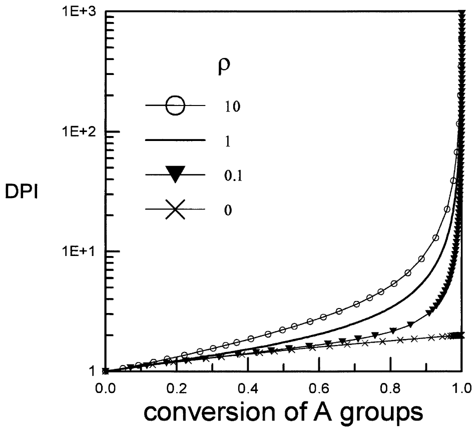


Fig. 3. PDI versus conversion of A groups for the systems with various rate constant ratios, ρ.

zero, no dendritic structures can be formed, and the PDI of this linear stepwise polymerization is $1 + \alpha(\mathrm{A})$. Therefore, it converges to be two at the complete conversion [18]. The PDI calculated by this kinetic model is higher than that simulated using the Monte Carlo method, which considered the bonded and non-bonded interactions between the segments in the finite cubic with 1000 monomers or repeat units [32].

The structure forms of the linear and dentritic units are $\sim\mathrm{a}{-}\!\!<^{\mathrm{b}\sim}_{\mathrm{B}'}$ and $\sim\mathrm{a}{-}\!\!<^{\mathrm{b}\sim}_{\mathrm{b}\sim}$, respectively. Figs. 4–6 show the substitution effects on the changes in the number of linear (NL) and dendritic units (ND) and the number of terminal units exclusive of monomers (NT′) with conversion, respectively. Both NL and ND increase with conversion. With a higher value of ρ, there is an increase in the opportunity of the reaction between the A group and linear $\sim\mathrm{a}{-}\!\!<^{\mathrm{b}\sim}_{\mathrm{B}'}$ unit. Consequently, ND value increases, whereas NL decreases. Furthermore, as the value of ρ decreases, the consumption rate of the monomer during polymerization increases, since the monomer having two unreacted B groups can readily react with another molecule (see Fig. 7).

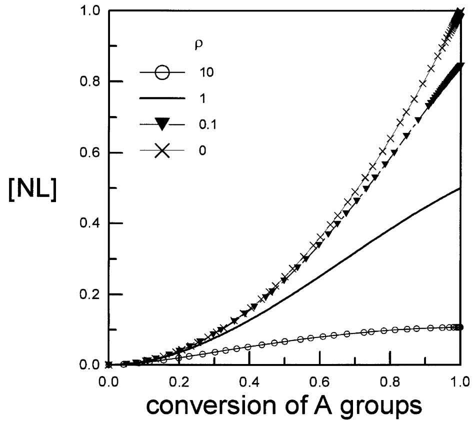


Fig. 4. Dependence of the number of linear units on conversion at various rate constant ratios, ρ ([NL] = NL/the initial number of A groups).

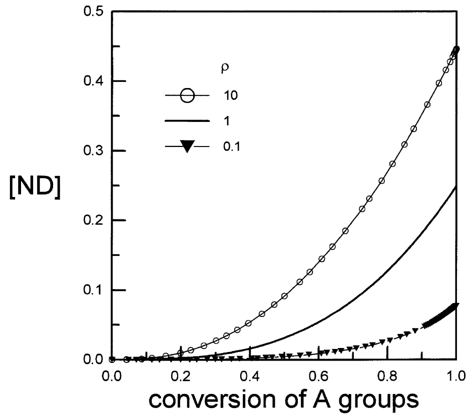


Fig. 5. Dependence of the number of dendritic units on conversion at various rate constant ratios, ρ ([ND] = ND/the initial number of A groups).

The degree of branching, DB, is a very important structural parameter in characterizing the hyperbranched polymers. Hawker and Frechet defined the degree of branching [13]

$$\mathrm{DB} = \frac{\mathrm{ND} + \mathrm{NT}}{\text{total number of units}} \tag{13}$$

where NT is the number of terminal units including monomer, $\sim\mathrm{a}{-}\!\!<^{\mathrm{B}}_{\mathrm{B}}$ and $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{B}}$. The DB defined above is generally overestimated for small molecules, for example, according to Eq. (13), the DB of AB_2 monomer always takes the highest value of one. Consequently, Holter and Frey [22] suggested a modified degree of branching, DB(HF), which is based on the actual number over the maximum possible number of dendritic units. Another parameter, the average number of branches (ANB) is defined as the deviation from the linear direction per non-terminal unit [23]. The definitions of the DB(HF) and ANB for the polymerization of AB_2 monomers are given by the following equations:

$$\mathrm{DB(HF)} = \frac{2\mathrm{ND}}{2\mathrm{ND} + \mathrm{NL}} = \frac{\mathrm{G}(5)}{\mathrm{G}(5) + 0.5\mathrm{G}(4)} \tag{14}$$

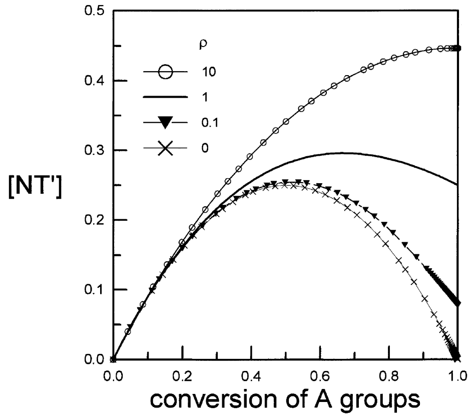


Fig. 6. Dependence of the number of terminal units exclusive of monomers on conversion at various rate constant ratios, ρ ([NT′] = NT′/the initial number of A groups).

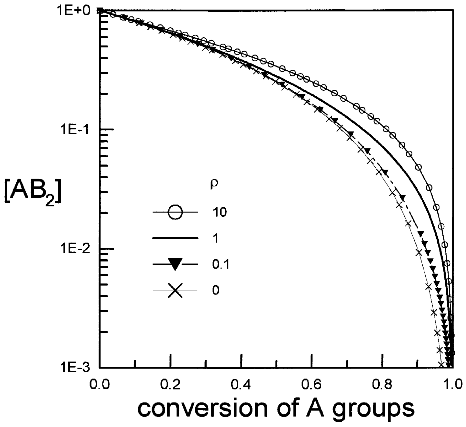


Fig. 7. Dependence of the number of monomers on conversion at various rate constant ratios, ρ ($[AB_2]$ = the number of monomers/the initial number of A groups).

$$\mathrm{ANB} = \frac{\mathrm{ND}}{\mathrm{ND} + \mathrm{NL}} = \frac{G(5)}{G(5) + G(4)} \tag{15}$$

Muller and Yan [26] also suggested the use of the fraction of branch points, FB, to characterize the hyperbranched polymers.

$$\mathrm{FB} = \frac{\mathrm{ND}}{(\text{total number of units}) - (\text{number of monomers})} = \frac{G(5)}{G(2) + G(3) + G(4) + G(5) + G(6)} \tag{16}$$

From the equations mentioned above, the increase of the degree of branching, DB(HF), with conversion can be calculated from the numbers of the linear and dendritic units, and the results are shown in Fig. 8. The significance of the substitution effect on the degree of branching of the hyperbranched polymers is further shown in Fig. 9. When the system has a ρ value less than one, the growth of the dendritic units is retarded, and consequently the degree of branching at full conversion is lower than that without the substitution effect ($\rho = 1$). On the other hand, the formation of the dendritic units becomes more favor for the system with a higher rate constant ratio, and the final degree of branching increases with an increase of the ρ value.

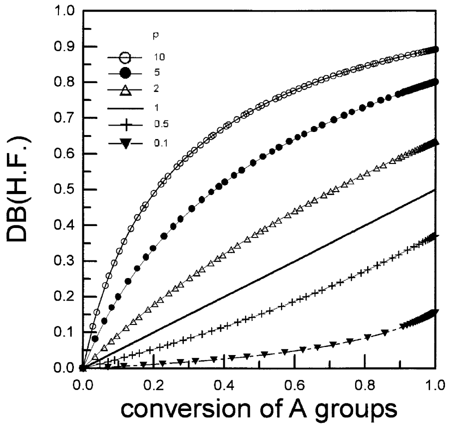


Fig. 8. Dependence of the degree of branching of the hyperbranched polymers on conversion at various rate constant ratios, ρ.

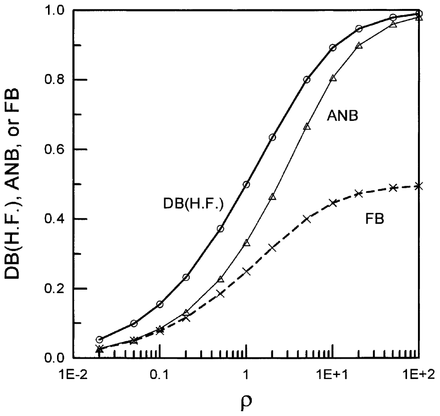


Fig. 9. Dependence of the final DB(HF), ANB, and FB of the hyperbranched polymers on the reactivity ratio, ρ.

4. Conclusion

This work has extended the generating function method to elucidate the growth of hyperbranched polymers formed by the polymerization of an AB_2 monomer. Use of this kinetic model revealed that the substitution effect causes different profiles of the weight-average degree of polymerization and the degree of branching of the hyperbranched polymers when compared to the case of equal reactivity for the two B_2 groups. When the substitution effect causes an increase in the rate constant after one of the B_2 groups has reacted during polymerization, a broader MWD and a higher degree of branching of the hyperbranched polymer are observed.

Acknowledgements

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Appendix A. Generating function method

The generating function method is applied to obtain the relationship between the average molecular weight and the reaction time. First, a generating function H, is defined

$$H(\tau, \omega_{j\ (j=1,2,\dots,n+1)}) = \sum_{\text{all } E} \left(\prod_{j=1}^{n+1} \omega_j^{e_j} \right) [E] \tag{A1}$$

where ω_j is a dummy variable, and H is a function of τ and ω_j.

Eq. (11) can be multiplied by $\sum_{\text{all } E} \left(\prod_{j=1}^{n+1} \omega_j^{e_j} \right)$ and summed over E to yield,

$$\frac{\partial H}{\partial \tau} = \sum_{i=1}^{m} k_i^{l} (H_{x_{i1}} H_{x_{i2}} x_{i3} x_{i4} - x_{i1} H_{x_{i1}} H_{i2} - x_{i2} H_{x_{i2}} H_{i1}) \tag{A2}$$

where $m = 12$, and $n = 6$ in this study, and

$$x_{ij} = \omega_J \; for \; b_{ij} = J$$

$$H_{x_{ij}} \equiv \frac{\partial H}{\partial x_{ij}}$$

$$H_{ij} \equiv H_{x_{ij}} (\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

that is, if $\mathrm{G}(b_{ij}) = \mathrm{G}(J)$,

$$b_{ij} = J$$

$$x_{ij} = \omega_J$$

$$\frac{\partial H}{\partial x_{ij}} = \frac{\partial H}{\partial \omega_J} = H_{\omega_J}$$

$$H_{ij} = H_{\omega_J} (\omega_{q\ (q=1,2,\dots,n+1)} = 1) \equiv H_J$$

By setting all dummy variables, $\omega_{q\ (q=1,2,\dots,n+1)}$ to 1, Eq. (A2) can be written as

$$\frac{\partial H^*}{\partial \tau} = \sum_{i=1}^{m} k_i^{l} (-H_{i1} H_{i2}) \tag{A3}$$

where $H^* = H(\omega_{q\ (q=1,2,\dots,n+1)} = 1)$. Furthermore, the partial derivatives of H along $\omega_{q\ (q=1,2,\dots,n+1)} = 1$ can be obtained by differentiating Eq. (A2) with respect to ω_r, or to both ω_r and ω_s

$$\frac{\partial H_r}{\partial \tau} = \sum_{i=1}^{m} k_i^{l} H_{i1} H_{i2} \left(\frac{\partial x_{i3} x_{i4}}{\partial \omega_r} - \frac{\partial x_{i1}}{\partial \omega_r} - \frac{\partial x_{i2}}{\partial \omega_r} \right) \tag{A4}$$

$$(\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

$$\begin{aligned} \frac{\partial H_{r,s}}{\partial \tau} = \sum_{i=1}^{m} k_i^{l} \Bigg[& H_{i1,r} H_{i2,s} + H_{il,s} H_{i2,r} + (H_{i1,r} H_{i2} \\ & + H_{i1} H_{i2,r}) \left(\frac{\partial x_{i3} x_{i4}}{\partial \omega_s} \right) + (H_{i1,s} H_{i2} + H_{i1} H_{i2,s}) \left(\frac{\partial x_{i3} x_{i4}}{\partial \omega_r} \right) \\ & + (H_{i1} H_{i2}) \left(\frac{\partial^2 x_{i3} x_{i4}}{\partial \omega_r \partial \omega_s} \right) - \left(\frac{\partial x_{i1}}{\partial \omega_r} H_{i1,s} + \frac{\partial x_{i1}}{\partial \omega_s} H_{i1,r} \right) H_{i2} \\ & - \left(\frac{\partial x_{i2}}{\partial \omega_r} H_{i2,s} + \frac{\partial x_{i2}}{\omega_s} H_{i2,r} \right) H_{i1} \Bigg] \quad (\omega_{q\ (q=1,2,\dots,n+1)} = 1) \end{aligned} \tag{A5}$$

where

$$H_r = \frac{\partial H}{\partial \omega_r} (\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

$$H_{r,s} = H_{s,r} = \frac{\partial^2 H}{\partial \omega_r \partial \omega_s} (\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

$$H_{ij,r} = H_{r,ij} = \frac{\partial^2 H}{\partial x_{ij} \partial \omega_r} (\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

$$H_{ij,s} = H_{s,ij} = \frac{\partial^2 H}{\partial x_{ij} \partial \omega_s} (\omega_{q\ (q=1,2,\dots,n+1)} = 1)$$

and the initial conditions are

$$H^*(\tau = 0) = \sum_{\text{all } E} [E]_0 \tag{A6}$$

$$H_r^*(\tau = 0) = \sum_{\text{all } E} e_r [E]_0 \tag{A7}$$

$$H_{r,s}^*(\tau = 0) = \sum_{\text{all } E} e_r e_s [E]_0, \qquad for \; r \neq s \tag{A8}$$

$$H_{r,r}^*(\tau = 0) = \sum_{\text{all } E} e_r (e_r - 1) [E]_0 \tag{A9}$$

$$[E]_0 = [E](\tau = 0) \tag{A10}$$

This set of ordinary differential equations, Eqs. (A3)–(A5), dependent on variable τ, can be solved by the Runge-Kutta method to determine $H^*(\tau)$, $H_r(\tau)$, and $H_{r,s}(\tau)$. The ath moment of the MWD is defined as

$$M_a = \left(\frac{N_0}{N_T} \right) \sum_{\text{all } E} W^a(E) [E] \tag{A11}$$

where $\mathrm{N_T}$ is the total number of molecules in the reaction system, and *W(E)* is the molecular weight of isomer, $\langle E \rangle$. The zeroth, first, and second moment of MWD can be calculated using the generating function:

$$M_0 = \left(\frac{N_0}{N_T} \right) H^* \tag{A12}$$

$$M_1 = \left(\frac{N_0}{N_T} \right) H_{n+1} \tag{A13}$$

$$M_2 = \left(\frac{N_0}{N_T}\right)(H_{n+1,n+1} + H_{n+1}) \tag{A14}$$

The number average and weight average molecular weights, $\bar{M}_n$, and $\bar{M}_w$, are obtained:

$$\bar{M}_n = \frac{M_1}{M_0} \tag{A15}$$

$$\bar{M}_w = \frac{M_2}{M_1} \tag{A16}$$

The conversion of G(J) units can also be calculated as

$$\text{Conversion of } \mathrm{G}(J) = 1 - N(\mathrm{G}(J))/N_0(\mathrm{G}(J))$$

$$= 1 - \sum_{\text{all } E} e_J[E] = 1 - H_J \tag{A17}$$

where $\mathrm{N}_0(\mathrm{G}(J)) = N(\mathrm{G}(J))$ at $\tau = 0$.

The relationships among the average molecular weight, conversion, and reaction time can be calculated by the following algorithm:

1. Calculate the initial conditions, $H^*(0)$, $H_r(0)$, and $H_{r,s}(0)$, from the concentrations of the reactants at $\tau = 0$, according to Eqs. (A6)–(A10).
2. Set $\tau \leftarrow \tau + \Delta\tau$, where $\Delta\tau$ is the specified step time.
3. Solve the set of ODEs, Eqs. (A3)–(A5), and obtain the values of $H^*(\tau)$, $H_r(\tau)$, and $H_{r,s}(\tau)$, by the Runge-Kutta method or other solvers.
4. Calculate the average molecular weights and conversions according to Eqs. (A15)–(A17).
5. Repeat procedures 2–4 until the specified time has reached.

References

[1] Kim YH, Webster OW. Macromolecules 1992;25:5561.
[2] Jikei M, Fujii K, Kakimoto M-A. J Polym Sci, Part A: Polym Chem 2001;39:3304.
[3] Emrick T, Chang H-T, Frechet JMJ. J Polym Sci, Part A: Polym Chem 2000;38:4850.
[4] Shi WF, Ranby B. J Appl Polym Sci 1996;59:1951.
[5] Uhrich K. Trends Polym Sci 1997;5:388.
[6] Rannard S, Davis N. Polymer Int 2000;49:1002.
[7] Johansson M, Malmstrom E, Hult A. J Polym Sci, Part A: Polym Chem 1993;31:619.
[8] Frechet JMJ, Henmi M, Gitsov I, Aoshima S, Leduc M, Grubbs RB. Science 1995;269:1080.
[9] Liu H, Nasman JH, Skrifvars M. J Polym Sci, Part A: Polym Chem 2000;38:3074.
[10] Voit B. J Polym Sci, Part A: Polym Chem 2000;38:2505.
[11] Hult A, Johansson M, Malmstrom E. Adv Polym Sci 1999;143:1.
[12] Nguyen C, Hawker CJ, Miller RD, Huang E, Hedrick JL, Gauderon R, Hilborn JG. Macromolecules 2000;33:4281.
[13] Hawker CJ, Lee R, Frechet JMJ. J Am Chem Soc 1991;113:4583.
[14] Yang Y, Zhang H, He J. Macromol Theor Simul 1995;4:953.
[15] Stockmayer WH. J Chem Phys 1943;11:45.
[16] Stockmayer WH. J Chem Phys 1944;12:125.
[17] Flory PJ. J Am Chem Soc 1952;74:2718.
[18] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953.
[19] Gordon M. Proc R Soc Lond 1962;A268:240.
[20] Gordon M, Scantlebury GR. Proc R Soc Lond 1966;A292:380.
[21] Gordon M, Scantlebury GR. Trans Faraday Soc 1964;6:604.
[22] Holter D, Burgath A, Frey H. Acta Polym 1997;48:30.
[23] Holter D, Frey H. Acta Polym 1997;48:298.
[24] Frey H, Holter D. Acta Polym 1999;50:67.
[25] Beginn U, Drohmann C, Moller M. Macromolecules 1997;30:4112.
[26] Yan D, Muller AHE, Matyjaszewski K. Macromolecules 1997;30:7024.
[27] Yan D, Zhou Z. Macromolecules 1999;32:819.
[28] Zhou Z, Yan D. Polymer 2000;41:4549.
[29] Cheng KC, Wang LY. Macromolecules 2002;35:5657.
[30] Dusek K. Adv Polym Sci 1985;75:113.
[31] Miller DR, Macosko CW. Macromolecules 1980;13:1063.
[32] Jo WH, Lee YU. Macromol Theor Simul 2001;10:225.
[33] Widmann AH, Davies GR. Comput Theor Polym Sci 1998;8:191.
[34] Galina HA, Szustalewicz A. Macromolecules 1989;22:3124.
[35] Galina HA, Szustalewicz A. Macromolecules 1990;23:3833.
[36] Cheng KC, Chiu WY. Macromolecules 1993;26:4658.
[37] Cheng KC, Chiu WY. Macromolecules 1993;26:4665.
[38] Cheng KC. J Polym Sci, Part B: Polym Phys 1998;36:2339.
[39] Dusek K, Somvarsky J, Smrckova M, Simonsick Jr. WJ, Wilczek L. Polym Bull 1999;42:489.
[40] Cameron C, Fawcett AH, Hetherington CR, Mee RAW, Mcbride FV. J Chem Phys 1998;108:8235.